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# The Hydrodynamics of Particles Suspended in a Melt with the Self-Consistent Concentration Field of an Admixture (Part I)

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**Abstract**—Small particles in the suspended state form in the nonuniform concentration field of admixture components as a result of steel deoxidation in melts. The hydrodynamic regimes of motion of particles interacting with changing concentration gradients occur in these conditions. A hydrodynamic theory of such self-consistent motion is constructed in the present paper. A relation determining the dependence of the velocity of relative motion of the particle–melt continuum on the gradient of the admixture concentration is obtained. © 1998 Elsevier Science Ltd. All rights reserved.

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## INTRODUCTION

The hydrodynamic systems, which are melts of iron with suspended small corundum particles of typical sizes $\sim$ 1–40 $\mu$m and more, are of interest in the metallurgic technology. Besides, in such systems, a melt can contain a surfactant (for example, oxygen) as an admixture. The hydrodynamic behavior of the admixture and small particles deserves special attention, because removal of the admixture and surfactants from melts is the main problem of metallurgy. Nonuniform adsorption of the surfactant at the surface of particles in the zone of the spatial gradient of the surfactant dissolved in the melt is an effective mechanism of removing admixtures from melts. In these conditions, hydrodynamic transport of particles with a self-consistent change in the spatial concentration of the surfactant takes place. Experimental evidence for the realization of this mechanism of hydrodynamic transport of macroscopic particles can be found in [1]. The problem of motion of a liquid drop in the field of constant concentration gradient has been solved in [2]. The purpose of the present paper is to obtain the hydrodynamic equations for admixture transport based on the mechanism described.

Let $M_c$ be the mass of a system representing a melt with particles distributed in it, and let $M_1$ be the mass of an admixture in the melt and at the surface of the particles. If the relative motion of the particles and the melt is absent, then the first law of thermodynamics for the system with admixture can be written in the form

$$de_o = T\,ds - p\,dV + \mu_c\,dM_c + \tilde{\mu}_1\,dM_1 + \sigma\,d\Sigma. \tag{1}$$

Here, $e_o$ is the internal energy; $T$ is the temperature; $s$ is the entropy; $p$ is the pressure; $\Sigma$ is the total surface of all particles, with $\Sigma = \varsigma N$, $\varsigma$ is the area of one particle, $N$ is the number

of particles in the volume $V$; $\sigma$ is the surface tension. In the presence of relative motion of the melt and the particles, a thermodynamically nonequilibrium system is generated. The first law of thermodynamics for this system is obtained from (1)

$$de_\circ = T\,ds - p\,dV + \mu_c\,dM_c + \tilde{\mu}_1\,dM_1 + \sigma\,d\Sigma + (\mathbf{u}-\mathbf{v})\,d\mathbf{I}_\circ, \tag{2}$$

where $\mathbf{I}_\circ$ is the relative momentum of the particle–liquid continuum. The thermodynamic nonequilibrium state is due to the hydrodynamic separation of two continua: the melt with the velocity $\mathbf{v}$, and the continuum of particles, the velocity of which is $\mathbf{u}$. Since the macroscopic volumes of the systems being considered are characterized by the spatial gradients, one should pass, in formula (2), on to the corresponding densities

$$e_\circ = E_\circ V, \qquad s = SV, \qquad M = \rho V, \qquad M_1 = \rho_1 V, \qquad \Sigma = \varsigma J V, \qquad \mathbf{I}_\circ = \mathbf{j}_\circ V,$$

after which the first law of thermodynamics

$$dE_\circ = T\,dS + \mu_c\,d\rho + \mu_1\,d\rho_1 + \varsigma\sigma\,dJ + (\mathbf{u}-\mathbf{v})\,d\mathbf{j}_\circ \tag{3}$$

can characterize a locally nonequilibrium element of the continuum. In (3), $\mu_1 = \tilde{\mu}_1 - \mu_c$, $J$ is the number of particles in the unit volume. Introducing the concentration $c = \rho_1/\rho$, it is convenient to represent (3) in the form

$$dE_\circ = T\,dS + \mu\,d\rho + \rho\mu_1\,dc + \varsigma\sigma\,dJ + (\mathbf{u}-\mathbf{v})\,d\mathbf{j}_\circ, \tag{4}$$

where

$$\mu = \mu_c + c\,(\tilde{\mu}_1 - \mu_c)\,.$$

Simultaneously with (3), we obtain an expression for the pressure

$$p = -E_\circ + TS + \mu_c\rho + \mu_1\rho_1 + \varsigma\sigma J + (\mathbf{u}-\mathbf{v})\,d\mathbf{j}_\circ,$$

the differential of which is calculated using (3)

$$dp = S\,dT + \rho\,d\mu_c + \rho_1\,d\mu_1 + \varsigma J\,d\sigma + \mathbf{j}_\circ\,d\,(\mathbf{u}-\mathbf{v})\,. \tag{5}$$

## REVERSIBLE EQUATIONS OF MOTION

Formula (3) characterizes the local nonequilibrium state of the particle continuum and the melt continuum moving relative to each other. Each of the continua contains a surfactant. The spatial variation of the thermodynamic variables of (3) is described by the conservation laws

$$\begin{gathered}
\frac{\partial\rho_1}{\partial t} + \operatorname{div}\,(\rho_1\mathbf{v} + \mathbf{D}_\circ) = 0, \qquad \frac{\partial J}{\partial t} + \operatorname{div}\,(J\mathbf{v} + \mathbf{J}_\circ) = 0, \\
\frac{\partial\rho}{\partial t} + \operatorname{div}\,(\rho\mathbf{v} + \mathbf{j}_\circ) = 0, \qquad \frac{\partial S}{\partial t} + \operatorname{div}\,(S\mathbf{v} + \mathbf{F}_\circ) = 0, \\
\frac{\partial j_i}{\partial t} + \partial_k(\rho v_i v_k + v_i j_{\circ,k} + v_k j_{\circ,i} + \Pi_{\circ,ik}) = 0, \\
\frac{\partial E}{\partial t} + \partial_i\left[Q_{\circ,i} + \left(\frac{\rho\mathbf{v}^2}{2} + \mathbf{v}\mathbf{j}_\circ + E_\circ\right)v_i + + \frac{\mathbf{v}^2}{2}j_{\circ,i} + \Pi_{\circ,ki}v_k\right] = 0,
\end{gathered} \tag{6}$$

in which

$$E = E_\circ + \frac{\rho\mathbf{v}^2}{2} + \mathbf{v}\mathbf{j}_\circ, \qquad \mathbf{j} = \mathbf{j}_\circ + \rho\mathbf{v}. \tag{7}$$

The structure of fluxes in (6) is due to the Galilei invariance of the conservation laws [3]. The fluxes with zero subscripts in (6) are the Galilei invariants and must be determined. As an

additional equation for the motion of liquid, we choose a quasilinear equation coinciding in its form with the continual form of the Newtonian equation and satisfying identically the conditions of thermodynamic equilibrium [4]

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v}, \nabla)\mathbf{v} = \alpha \nabla \mu_c + \beta \nabla T + \gamma \nabla \mu_1 + \omega \nabla(\varsigma\sigma). \tag{8}$$

Equations (6),(8) should be made consistent with each other and with the first law of thermodynamics (3). For this purpose, we differentiate the first relation from (7) with respect to time and, using (3), obtain

$$\frac{\partial E}{\partial t} = T\frac{\partial S}{\partial t} + \left(\mu_c + \frac{\mathbf{v}^2}{2} - \mathbf{vu}\right)\frac{\partial \rho}{\partial t} + \mu_1 \frac{\partial \rho_1}{\partial t} + (\mathbf{j} - \rho\mathbf{u})\frac{\partial \mathbf{v}}{\partial t} + \mathbf{u}\frac{\partial \mathbf{j}}{\partial t} + \varsigma\sigma\frac{\partial J}{\partial t}. \tag{9}$$

Since the conservation laws (6) and the equations of motion (8) are satisfied, equality (9) must be satisfied identically. Substituting the time derivatives from (6) and (8) into (9), we obtain

$$\begin{aligned}
&\partial_i[Q_{o,i} - TF_{o,i} - \mu_c j_{o,i} - \varsigma\sigma J_{o,i} - \mu_1 D_{o,i} - (\Pi_{o,ki} - p\delta_{ki} - j_{o,k}w_i)w_k - (\mathbf{j}_o\mathbf{w})w_i] \\
&= \nabla T[-\mathbf{F}_o - \beta(\mathbf{j} - \rho\mathbf{u}) + S\mathbf{w}] - (1+\alpha)\nabla\mu_c(\mathbf{j} - \rho\mathbf{u}) + \nabla(\varsigma\sigma)[-\mathbf{J}_o - \omega(\mathbf{j} - \rho\mathbf{u}) + J\mathbf{w}] \\
&+\nabla\mu_1[-\mathbf{D}_o - \gamma(\mathbf{j} - \rho\mathbf{u}) + \rho_1\mathbf{w}] - (\Pi_{o,ik} - p\delta_{ik} - j_{o,i}w_k)\partial_k u_i + (w_i j_{o,k} - w_k j_{o,i})\partial_k v_i.
\end{aligned}$$

Here $\mathbf{w} = \mathbf{u} - \mathbf{v}$. In the absence of energy dissipation, the invariant flows must not depend on the gradients. Besides, the invariant flows must depend on the velocities only via the Galilei invariant $\mathbf{w}$. These conditions can be satisfied, if we set [5]

$$\begin{gathered}
1 + \alpha = 0, \qquad \mathbf{F}_o + \beta(\mathbf{j} - \rho\mathbf{u}) - S\mathbf{w} = 0, \qquad \mathbf{J}_o + \omega(\mathbf{j} - \rho\mathbf{u}) - J\mathbf{w} = 0, \\
\mathbf{D}_o + \gamma(\mathbf{j} - \rho\mathbf{u}) - \rho_1\mathbf{w} = 0, \qquad \Pi_{o,ik} = p\delta_{ik} + j_{o,i}w_k, \\
\mathbf{Q}_o = T\mathbf{F}_o + \mu_c\mathbf{j}_o + \varsigma\sigma\mathbf{J}_o + \mu_1\mathbf{D}_o + (\mathbf{j}_o\mathbf{w})\mathbf{w},
\end{gathered} \tag{10}$$

in the derivation of the latter relations, it is taken into account that

$$\rho = \rho_s + \rho_l, \qquad \mathbf{j}_o = \rho_s\mathbf{w}, \qquad \mathbf{j} - \rho\mathbf{u} = -\rho_l\mathbf{w}.$$

Equality (5) makes it possible to write equation (8) in the following form:

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v}, \nabla)\mathbf{v} = -\frac{\nabla p}{\rho} + \left(\beta + \frac{S}{\rho}\right)\nabla T + \left(\gamma + \frac{\rho_1}{\rho}\right)\nabla\mu_1 + \varsigma\left(\omega + \frac{J}{\rho}\right)\nabla\sigma + \frac{\rho_s}{2\rho}\nabla\mathbf{w}^2.$$

The fluxes $\mathbf{F}_o$, $\mathbf{J}_o$, $\mathbf{D}_o$ must be uniquely determined on a physically realistic background. Particles in the liquid must be transported with the velocity $\mathbf{u}$, because no flux of particles must occur in the liquid. Hence,

$$\frac{\partial J}{\partial t} + \operatorname{div}(J\mathbf{u}) = 0.$$

This determines the flux value $\mathbf{J}_o = J\mathbf{w}$ and, as a consequence, we obtain $\omega = 0$. The theory must give correct passages to the limit in the absence of surface tension. This is possible, if we choose

$$\beta = -\frac{S}{\rho}, \qquad \gamma = -\frac{\rho_1}{\rho}.$$

Consequently,

$$\mathbf{F}_o = \frac{\rho_s}{\rho}S\mathbf{w}, \qquad \mathbf{D}_o = \frac{\rho_s}{\rho}\rho_1\mathbf{w}.$$

At such choice of fluxes, introduction of an admixture into the system does not change the equations of motion, which corresponds to the main property of the classical one-velocity theory

of solutions [3]. After determining the fluxes in this way, we obtain the formulation of the reversible variant of the hydrodynamic theory

$$\frac{\partial J}{\partial t} + \operatorname{div}(J\mathbf{u}) = 0, \qquad \frac{\partial \rho}{\partial t} + \operatorname{div}\mathbf{j} = 0, \qquad \frac{\partial \rho_1}{\partial t} + \operatorname{div}\left(\frac{\rho_1}{\rho}\mathbf{j}\right) = 0,$$

$$\frac{\partial S}{\partial t} + \operatorname{div}\left(\frac{S}{\rho}\mathbf{j}\right) = 0, \qquad \frac{\partial j_i}{\partial t} + \partial_k(\rho_s u_i u_k + \rho_l v_i v_k + p\delta_{ik}) = 0, \tag{11}$$

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v}, \nabla)\,\mathbf{v} = -\frac{\nabla p}{\rho} + \varsigma\frac{J}{\rho}\nabla\sigma + \frac{\rho_s}{2\rho}\nabla\mathbf{w}^2.$$

The latter two equations of the system lead to the equation

$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u}, \nabla)\,\mathbf{u} = -\frac{\nabla p}{\rho} - \frac{\rho_l}{\rho_s}\varsigma\frac{J}{\rho}\nabla\sigma - \frac{\rho_l}{2\rho}\nabla\mathbf{w}^2 - \frac{\mathbf{w}}{\rho_s}\left[\frac{\partial \rho_s}{\partial t} + \operatorname{div}(\rho_s\mathbf{u})\right]. \tag{12}$$

Subtracting the latter equation of system (11) from equation (12), we obtain

$$\frac{\partial \mathbf{w}}{\partial t} + (\mathbf{w}, \nabla)\,\mathbf{w} + \frac{1}{2}\nabla\mathbf{w}^2 + (\mathbf{w}, \nabla)\mathbf{v} + (\mathbf{v}, \nabla)\mathbf{w} = -\varsigma\frac{J}{\rho_s}\nabla\sigma - \frac{\mathbf{w}}{\rho_s}\left[\frac{\partial \rho_s}{\partial t} + \operatorname{div}(\rho_s\mathbf{u})\right]. \tag{13}$$

Equation (13) suggests an important fact: the presence of the gradient of surface tension in the system is associated with the existence of the relative velocity of motion of the liquid and the particle continuum, i.e., the relation between $\nabla\sigma$ and $\mathbf{w}$ is of locally kinetic character.

## IRREVERSIBLE EQUATIONS OF MOTION

The total system of equations taking into account the dissipative effects is obtained from (11) by adding the irreversible fluxes to the corresponding reversible fluxes of the conservation laws

$$\frac{\partial J}{\partial t} + \operatorname{div}(J\mathbf{u}) = 0, \qquad \frac{\partial \rho}{\partial t} + \operatorname{div}\mathbf{j} = 0,$$

$$\frac{\partial \rho_1}{\partial t} + \operatorname{div}\left[\frac{\rho_1}{\rho}\mathbf{j} - \frac{\lambda_1}{T}(\mathbf{j} - \rho\mathbf{u}) + \mathbf{L}_1\right] = 0,$$

$$\frac{\partial S}{\partial t} + \operatorname{div}\left[\frac{S}{\rho}\mathbf{j} - \frac{\lambda}{T}(\mathbf{j} - \rho\mathbf{u}) + \frac{\lambda_1\mu_1}{T^2}(\mathbf{j} - \rho\mathbf{u}) + \frac{\mathbf{q}}{T} - \frac{\mu_1\mathbf{L}_1}{T}\right] = \frac{R}{T}, \tag{14}$$

$$\frac{\partial j_i}{\partial t} + \partial_k(\rho_s u_i u_k + \rho_l v_i v_k + p\delta_{ik} + \pi_{ik}) = 0,$$

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v}, \nabla)\mathbf{v} = -\frac{\nabla p}{\rho} + \varsigma\frac{J}{\rho}\nabla\sigma + \frac{\rho_s}{2\rho}\nabla\mathbf{w}^2 + \lambda_1\nabla\left(\frac{\mu_1}{T}\right) + \lambda\frac{\nabla T}{T} + \mathbf{f},$$

$$\frac{\partial E}{\partial t} + \operatorname{div}(\mathbf{Q} + \mathbf{W}) = 0.$$

In equations (14), $R$ is the dissipative function, $\mathbf{q}$, $\mathbf{L}_1$, $\mathbf{W}$, and $\pi_{ik}$ are the irreversible flows, and $\mathbf{f}$ is the friction force. Equations (14) must satisfy identically the differential form (3), which is possible at a certain choice of the irreversible flows. To satisfy the differential form (4), we substitute the time derivatives of (14) into relation (9) and, after simplifications, we come to the equality

$$\partial_i\left[W_i - q_i + \lambda(j_i - \rho u_i) - \pi_{ik}v_i\right] = -R - \frac{\mathbf{q}}{T}\nabla T - T\mathbf{L}_1\nabla\left(\frac{\mu_1}{T}\right) - \frac{1}{2}\pi_{ik}\left(\partial_k v_i + \partial_i v_k\right) - (j_i - \rho u_i)\left(f_i + \frac{1}{\rho_l}\partial_k\pi_{ik}\right). \tag{15}$$

The left-hand side of the equation determines the irreversible energy flux

$$W_i = q_i - \lambda\,(j_i - \rho u_i) + \pi_{ik} v_i,$$

and the right-hand side determines the dissipative function

$$R = -(j_i - \rho u_i)\left(f_i + \frac{1}{\rho_l}\partial_k \pi_{ik}\right) - \frac{\mathbf{q}}{T}\nabla T - T\mathbf{L}_1 \nabla\left(\frac{\mu_1}{T}\right) - \frac{1}{2}\pi_{ik}\left(\partial_k v_i + \partial_i v_k\right).$$

It is necessary to bring the latter expression to the following standard form:

$$R = -(j_i - \rho u_i)\left(f_i + \frac{1}{\rho_l}\partial_k \pi_{ik}\right) - \frac{\mathbf{q}}{T}\nabla T - T\mathbf{L}_1 \nabla\left(\frac{\mu_1}{T}\right) - \frac{1}{2}A_{ik}\left(\partial_k v_i + \partial_i v_k - \frac{2}{3}\delta_{ik}\mathrm{div}\ \mathbf{v}\right) - a\,\mathrm{div}\ \mathbf{v},$$

$\pi_{ik} = A_{ik} + a\delta_{ik}$, $A_{\nu\nu} = 0$. The linear thermodynamic relations between the thermodynamic forces and the corresponding thermodynamic fluxes can be written, if we introduce the kinetic coefficients $B_{11}$, $B_{22}$, $B_{33}$, $B_{23}$, $\lambda$, $\lambda_1$, $\eta$, and $\zeta$,

$$\begin{aligned}
f_i + \frac{1}{\rho_l}\partial_k \pi_{ik} &= -B_{11}(j_i - \rho u_i) - \lambda\frac{\partial_i T}{T} - \lambda_1 \partial_i\left(\frac{\mu_1}{T}\right), \\
\mathbf{q} &= -\lambda(\mathbf{j} - \rho\mathbf{u}) - B_{22}\frac{\nabla T}{T} - B_{23}\nabla\left(\frac{\mu_1}{T}\right), \\
T\mathbf{L}_1 &= -\lambda_1(\mathbf{j} - \rho\mathbf{u}) - B_{23}\frac{\nabla T}{T} - B_{33}\nabla\left(\frac{\mu_1}{T}\right), \\
A_{ik} &= -\eta\left(\partial_k v_i + \partial_i v_k - \frac{2}{3}\delta_{ik}\mathrm{div}\ \mathbf{v}\right), \qquad a = -\zeta\mathrm{div}\ \mathbf{v}.
\end{aligned} \tag{16}$$

The dissipative function is a positive definite quadratic form

$$\begin{aligned}
R = B_{11}&\left[\mathbf{j} - \rho\mathbf{u} + \frac{\lambda}{B_{11}}\frac{\nabla T}{T} + \frac{\lambda_1}{B_{11}}\nabla\left(\frac{\mu_1}{T}\right)\right]^2 \\
&+ \left(B_{22} - \frac{\lambda^2}{B_{11}}\right)\left[\frac{\nabla T}{T} + \frac{B_{11}B_{23} - \lambda\lambda_1}{B_{11}B_{22} - \lambda^2}\nabla\left(\frac{\mu_1}{T}\right)\right]^2 \\
&+ \left[B_{33} - \frac{\lambda_1^2}{B_{11}} - \frac{\left(B_{23} - \lambda\lambda_1 B_{11}^{-1}\right)^2}{B_{22} - \lambda^2 B_{11}^{-1}}\right]\left[\nabla\left(\frac{\mu_1}{T}\right)\right]^2,
\end{aligned} \tag{17}$$

with

$$B_{11} \geq 0, \qquad B_{11}B_{22} \geq \lambda^2, \qquad \left(B_{11}B_{33} - \lambda_1^2\right)\left(B_{11}B_{22} - \lambda^2\right) \geq \left(B_{11}B_{23} - \lambda\lambda_1\right)^2.$$

Substituting fluxes (16) into equations (14), we obtain the following system of equations:

$$\begin{aligned}
&\frac{\partial J}{\partial t} + \mathrm{div}\,(J\mathbf{u}) = 0, \qquad \frac{\partial \rho}{\partial t} + \mathrm{div}\ \mathbf{j} = 0, \qquad \frac{\partial \rho_1}{\partial t} + \mathrm{div}\left(c_s\rho_s\mathbf{u} + c_l\rho_l\mathbf{v} + \tilde{\mathbf{L}}_1\right) = 0, \\
&\frac{\partial S}{\partial t} + \mathrm{div}\left(S_u\mathbf{u} + S_v\mathbf{v} + \frac{\tilde{\mathbf{q}}}{T} - \frac{\mu_1\tilde{\mathbf{L}}_1}{T}\right) = \frac{R}{T}, \\
&\frac{\partial j_i}{\partial t} + \partial_k\left[\rho_s u_i u_k + \rho_l v_i v_k + p\delta_{ik} - \eta\left(\partial_k v_i + \partial_i v_k - \frac{2}{3}\delta_{ik}\mathrm{div}\ \mathbf{v}\right) - \zeta\mathrm{div}\ \mathbf{v}\right] = 0, \\
&\frac{\partial v_i}{\partial t} + (\mathbf{v}, \nabla)v_i = -\frac{\partial_i p}{\rho} + \varsigma\frac{J}{\rho}\partial_i\sigma + \frac{\rho_s}{2\rho}\partial\mathbf{w}^2 - B_{11}(j_i - \rho u_i) \\
&\qquad + \frac{1}{\rho_l}\partial_k\left[\eta\left(\partial_k v_i + \partial_i v_k - \frac{2}{3}\delta_{ik}\,\mathrm{div}\ \mathbf{v}\right) + \zeta\mathrm{div}\ \mathbf{v}\right].
\end{aligned} \tag{18}$$

Here, we denote

$$c_s\rho_s = \frac{\rho_1}{\rho}\rho_s + \frac{2\lambda_1\rho_l}{T}, \qquad S_u = \frac{\rho_s}{\rho}S + \frac{2\lambda\rho_l}{\rho} - \frac{2\lambda_1\mu_1\rho_l}{T^2},$$

$$c_l\rho_l = \frac{\rho_1}{\rho}\rho_l - \frac{2\lambda_1\rho_l}{T}, \qquad S_v = \frac{\rho_s}{\rho}S - \frac{2\lambda\rho_l}{\rho} + \frac{2\lambda_1\mu_1\rho_l}{T^2},$$

$$\tilde{\mathbf{L}}_1 = -B_{23}\frac{\nabla T}{T^2} - \frac{B_{33}}{T}\nabla\left(\frac{\mu_1}{T}\right),$$

$$\tilde{\mathbf{q}} = -B_{22}\frac{\nabla T}{T} - B_{23}\nabla\left(\frac{\mu_1}{T}\right).$$

The system makes it possible to obtain an equation determining the velocity of the continuum of solid particles,

$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u}, \nabla)\mathbf{u} = -\frac{\nabla p}{\rho} - \frac{\rho_l}{\rho_s}\varsigma\frac{J}{\rho}\nabla\sigma - \frac{\rho_l}{2\rho}\nabla\mathbf{w}^2 + \frac{\rho_l}{\rho_s}B_{11}(\mathbf{j} - \rho\mathbf{u}) - \frac{\mathbf{w}}{\rho_s}\left[\frac{\partial\rho_s}{\partial t} + \operatorname{div}\,(\rho_s\mathbf{u})\right], \quad (19)$$

which, together with the equation

$$\begin{aligned}\frac{\partial v_i}{\partial t} + (\mathbf{v}, \nabla)v_i = &-\frac{\partial_i p}{\rho} + \varsigma\frac{J}{\rho}\partial_i\sigma + \frac{\rho_s}{2\rho}\partial_i\mathbf{w}^2 - B_{11}(j_i - \rho u_i)\\ &+ \frac{1}{\rho_l}\partial_k\left[\eta\left(\partial_k v_i + \partial_i v_k - \frac{2}{3}\delta_{ik}\operatorname{div}\mathbf{v}\right) + \zeta\operatorname{div}\mathbf{v}\right],\end{aligned} \quad (20)$$

determines the variation of $\mathbf{w}$

$$\begin{aligned}\frac{\partial w_i}{\partial t} + (\mathbf{w}, \nabla)w_i + \frac{1}{2}\partial_i\mathbf{w}^2 + (\mathbf{w}, \nabla)v_i + (\mathbf{v}, \nabla)w_i = &-\varsigma\frac{J}{\rho_s}\partial_i\sigma - \frac{w_i}{\rho_s}\left[\frac{\partial\rho_s}{\partial t} + \operatorname{div}\,(\rho_s\mathbf{u})\right]\\ -\frac{\rho_l}{\rho_s}\rho B_{11}w_i - \frac{1}{\rho_l}\partial_k&\left[\eta\left(\partial_k v_i + \partial_i v_k - \frac{2}{3}\delta_{ik}\operatorname{div}\mathbf{v}\right) + \zeta\operatorname{div}\mathbf{v}\right].\end{aligned} \quad (21)$$

For small velocities in the absence of the inertial and viscous effects, equation (21) gives an important result

$$\frac{\partial \mathbf{w}}{\partial t} + \frac{\rho_l}{\rho_s}\rho B_{11}\mathbf{w} = \varsigma\frac{J}{\rho_s}\nabla\sigma, \qquad B_{11} \geq 0.$$

The latter relation implies that the presence of the gradient of surface tension in the system generates the relative velocity of motion. In the absence of the gradient of surface tension, the velocity difference $\mathbf{w}_o$, since it has occurred, decays in accordance with the law

$$\mathbf{w} \sim \mathbf{w}_o e^{-t/\tau}, \qquad \tau = \frac{\rho_s}{\rho_l\rho B_{11}}.$$

The stationary regime of motion is described by the equation

$$\mathbf{w} = -\frac{\varsigma}{m}\tau\nabla\sigma. \quad (22)$$

The latter relation can be used to estimate the velocity of motion of an isolated particle in the field of constant gradient of the admixture concentration. This regime can be employed to estimate the constant $\tau$.

## ADSORPTION OF THE ADMIXTURE

In the general case, redistribution of an admixture at the surface of particles is caused by the presence of the admixture flux from the liquid to the surface of particles. It is seen from the equation

$$\frac{\partial}{\partial t}(c_s\rho_s + c_l\rho_l) + \operatorname{div}\left[\left(\frac{\rho_1}{\rho}\rho_s + \frac{2\lambda_1\rho_l}{T}\right)\mathbf{u} + \left(\frac{\rho_1}{\rho}\rho_l - \frac{2\lambda_1\rho_l}{T}\right)\mathbf{v} + \tilde{\mathbf{L}}_1\right] = 0, \tag{23}$$

$$\rho_1 = c_s\rho_s + c_l\rho_l,$$

that the absence of equal admixture concentrations in the liquid $c_l$ and in the particles $c_s$ is associated with the presence of the flux

$$\frac{2\lambda_1\rho_l}{T}\mathbf{w} \tag{24}$$

from the liquid to the particles. This flux is of kinetic nature and can be calculated from the consideration of the local stationary process, which causes the motion of particles as a result of nonuniform adsorption by the surface of particles in the field of the gradient of the admixture concentration.

A simple analysis of the stationary process of admixture adsorption from a moving liquid on the surface of particles can be made for a spherical particle of radius $a$. Let the particle be at rest, and let the solution flow run on it from infinity with the velocity $\tilde{\mathbf{u}} = (\tilde{u}, 0, 0)$. Let us place the particle at the center of the spherical system of coordinates, direct the axis $x$ colinearly to the velocity vector, and measure the angle $\theta$ from the axis $x$, so that at $r \to \infty$,

$$v_r = \tilde{u}\cos\theta, \qquad v_\theta \to -\tilde{u}\sin\theta. \tag{25}$$

The stationary field of low velocities of an incompressible liquid satisfies equations [3]

$$\begin{aligned}
\frac{\partial\tilde{p}}{\partial r} &= \frac{\partial^2 v_r}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2 v_r}{\partial\theta^2} + \frac{2}{r}\frac{\partial v_r}{\partial r} + \frac{\cot\theta}{r^2}\frac{\partial v_r}{\partial\theta} - \frac{2}{r^2}\frac{\partial v_\theta}{\partial\theta} - \frac{2v_r}{r^2} - \frac{2\cot\theta}{r^2}v_\theta,\\
\frac{\partial\tilde{p}}{\partial\theta} &= \frac{\partial^2 v_\theta}{\partial r^2} + \frac{1}{r^2}\frac{\partial^2 v_\theta}{\partial\theta^2} + \frac{2}{r}\frac{\partial v_\theta}{\partial r} + \frac{\cot\theta}{r^2}\frac{\partial v_\theta}{\partial\theta} + \frac{2}{r^2}\frac{\partial v_r}{\partial\theta} - \frac{v_\theta}{r^2\sin^2\theta},\\
\frac{\partial v_r}{\partial r} &+ \frac{1}{r}\frac{\partial v_\theta}{\partial\theta} + \frac{2v_r}{r} + \frac{v_\theta\cot\theta}{r} = 0.
\end{aligned} \tag{26}$$

Since tangential forces act on the liquid near the particle surface under nonuniform adsorption, the boundary conditions at the surface of a spherical particle should be written in the form

$$\begin{aligned}
v_\theta(r = a) &= v_\circ\sin\theta,\\
v_r(r = a) &= 0.
\end{aligned} \tag{27}$$

In this case, in accordance with the method taking into account the external driving force acting on a particle [2], we require vanishing of the total viscous force

$$\iint (P_{rr}\cos\theta - P_{r\theta}\sin\theta)\sin\theta\, d\theta\, d\varphi = 0. \tag{28}$$

Here the integral is taken over the surface of the particle; $P_{rr}$, $P_{r\theta}$ are the components of the tensor of momentum flux density. The solution to equation (26) satisfying conditions (25),(27),(28) has the form

$$v_r = 2v_\circ\left(\frac{a}{r} - 1\right)\cos\theta, \qquad v_\theta = 2v_\circ\left(1 - \frac{a}{2r}\right), \qquad \tilde{p} = p_\circ + 2\frac{a}{r}v_\circ\cos\theta. \tag{29}$$

Conditions (25) make it possible to relate the tangential velocity at the surface of the particle with the relative velocity of motion of the continua

$$w = 2v_\circ.$$

As we know the velocity field (29), we can calculate the admixture flux for the particle. The stationary distribution of the admixture concentration is described at the surface of the particle by the equation

$$v_r \frac{\partial \bar{c}}{\partial r} + \frac{v_\theta}{r} \frac{\partial \bar{c}}{\partial \theta} = D \frac{\partial^2 \bar{c}}{\partial r^2}. \tag{30}$$

In this equation, $\bar{c}$ is the volume concentration, $D$ is the diffusion coefficient. The angular term of the Laplacian is omitted in the right-hand side of the equation. The boundary conditions for equation (31) have the following form:

$$\bar{c}(r = \infty) = \bar{c}_l, \qquad \bar{c}(r = a) = \bar{c}_*, \qquad \bar{c}(r = a, \theta = 0) = \bar{c}_l. \tag{31}$$

The procedure of solving equation (30) is standard [2] and is realized by introducing the stream function

$$\psi = v_\circ \left(\frac{a}{r} - 1\right) r^2 \sin^2 \theta,$$

with

$$v_r = \frac{1}{r^2 \sin \theta} \frac{\partial \psi}{\partial \theta}, \qquad v_\theta = -\frac{1}{r \sin \theta} \frac{\partial \psi}{\partial r}.$$

In equation (30), it is recommended to take $\psi$, $\theta$ instead of the independent variables $r$, $\theta$, making formal substitution of the variables

$$\psi(r, \theta) = v_\circ \left(\frac{a}{r} - 1\right) r^2 \sin^2 \theta, \qquad \theta(r, \theta) = \theta.$$

In the new variables, we obtain the equation

$$\frac{v_\theta}{r} \left(\frac{\partial \bar{c}}{\partial \theta}\right)_\psi = D \left[\frac{\partial^2 \bar{c}}{\partial \psi^2} \left(\frac{\partial \psi}{\partial r}\right)^2 + \left(\frac{\partial \bar{c}}{\partial \psi}\right)_\theta \frac{\partial^2 \psi}{\partial r^2}\right]. \tag{32}$$

Solutions to equation (32) near the surface of the particle are of interest to us. Let us determine the small parameter in the explicit form

$$y = r - a$$

and determine, in (32), the term of the principal order with respect to $y$

$$\frac{\partial \bar{c}}{\partial \theta} = D a^3 v_\circ \sin^3 \theta \frac{\partial^2 \bar{c}}{\partial \psi^2}. \tag{33}$$

Equation (33) is supplemented by the boundary conditions

$$\bar{c}(\psi = \infty) = \bar{c}_l, \qquad \bar{c}(\psi = 0) = \bar{c}_*, \qquad \bar{c}(\psi = 0, \theta = 0) = \bar{c}_l.$$

Self-simulating solutions to the equation of "heat conductivity" (33) with these boundary conditions can be obtained easily

$$\bar{c} = \frac{2}{\sqrt{\pi}} (\bar{c}_l - \bar{c}_*) \int_0^\Omega e^{-x^2} dx + \bar{c}_*,$$

$$\Omega = \frac{awy\sin^2\theta}{2\sqrt{2Dwa^3\,(2/3 - \cos\theta + \cos^3\theta/3)}}. \tag{34}$$

Solution (34) makes it possible to calculate the density of the admixture flux for the particle [2]

$$D\left(\frac{\partial\bar{c}}{\partial y}\right)_{y=0} = \frac{D(\bar{c}_l - \bar{c}_*)}{\delta}, \qquad \delta = \sqrt{\frac{2\pi aD}{3w}}\sqrt{\frac{2+\cos\theta}{(1+\cos\theta)^2}}.$$

The average flux density for the particle is calculated by integrating the flux density over the surface of a spherical particle

$$\frac{1}{4\pi a^2}\int_0^\pi D\left(\frac{\partial\bar{c}}{\partial y}\right)_{y=0} 2\pi a^2\sin\theta\,d\theta = \sqrt{\frac{2Dw}{3\pi a}}\,(c_l - c_*)\,\rho_l^f, \tag{35}$$

where $c_l$, $c_*$ are the mass local concentrations, $\rho_l^f$ is the physical density of the melt. On the other hand, the flux obtained should be made consistent with formula (24)

$$\frac{2\lambda_1\rho_l}{T}w = \sqrt{\frac{2Dw}{3\pi a}}(c_l - c_*)\rho_l^f.$$

We find from the latter equality that

$$\lambda_1 = T\sqrt{\frac{D}{6\pi a}}\frac{\rho_l^f}{\rho_l}\frac{c_l - c_*}{\sqrt{w}}. \tag{36}$$

Since

$$c_s\rho_s = \frac{\rho_1}{\rho}\rho_s + \frac{2\lambda_1\rho_l}{T}, \qquad c_l\rho_l = \frac{\rho_1}{\rho}\rho_l - \frac{2\lambda_1\rho_l}{T},$$

we obtain, substituting $\lambda_1$ from (36),

$$c_s\rho_s = \frac{\rho_1}{\rho}\rho_s + \Lambda(c_l - c_*), \qquad c_l\rho_l = \frac{\rho_1}{\rho}\rho_l - \Lambda(c_l - c_*), \qquad \Lambda = \sqrt{\frac{2D}{3\pi a}}\frac{\rho_l^f}{\sqrt{w}}. \tag{37}$$

If the function $\Gamma(c_*)$ characterizes the adsorption properties of the particle surface, then, ignoring the mass of adsorbed oxygen at the surface of the particle, we can write

$$\rho_s = J\,[m + \varsigma\Gamma(c_*)] \approx Jm, \qquad \rho_l \approx \rho - Jm.$$

Using the definition $c = \rho_1/\rho$, we transform formula (37)

$$J\varsigma\Gamma(c_*) = cJm + \Lambda(c_l - c_*), \qquad c_l(\rho - Jm) = c(\rho - Jm) - \Lambda(c_l - c_*). \tag{38}$$

Equations (38) make it possible to determine the functions

$$c_l = c_l(J,\,\rho,\,c), \qquad c_* = c_*(J,\,\rho,\,c)$$

of the variables, which are included in the time derivatives in the conservation laws (18). At $Jm \ll \rho$ (this can be satisfied for particles of composition $Al_2O_3$ and a melt of Fe), we obtain

$$J\varsigma\Gamma(c_*) = \frac{\rho\Lambda}{\rho+\Lambda}(c - c_*) + cmJ. \tag{39}$$

If the adsorption properties of the surface are described by the Langmuir dependence

$$\Gamma(c_*) = \frac{kc_*}{1 + kc_*/\Gamma_\infty},$$

we obtain the dependencies

$$c_l = \frac{\rho}{\rho+\Lambda}c + \frac{\Lambda}{\rho+\Lambda}c_* = c_l(\rho, J, c), \qquad c_s = c + \frac{\rho}{Jm}\frac{\Lambda}{\rho+\Lambda}(c-c_*) = c_s(\rho, J, c), \tag{40}$$

in which $c_*$ satisfies the equation

$$c_*^2 + c_*\left[\frac{\Gamma_\infty}{k} - c + \Gamma_\infty J\varsigma\left(\frac{1}{\rho}+\frac{1}{\Lambda}\right)\right] - \frac{\Gamma_\infty}{k}c = 0.$$

To close system of equations (18), it is necessary to determine in the chemical potential $\mu_1$ from (18) the part, depending on the surface energy. For this, we represent the principal thermodynamic identity (4) in the form

$$\begin{aligned} d\Phi &= -S\,dT + \mu\,d\rho + \rho\mu_1\,dc - \varsigma J\,d\sigma - \mathbf{j}_\circ\,d\mathbf{w}, \\ \Phi &= E_\circ - TS - \varsigma\sigma J - \mathbf{w}\mathbf{j}_\circ. \end{aligned} \tag{41}$$

The adsorption Langmuir dependence corresponds to the dependence of the surface tension on the concentration

$$\sigma = \sigma_\circ - \Gamma_\infty RT\ln\left(1 + \frac{k}{\Gamma_\infty}c_*\right). \tag{42}$$

We obtain from the formula presented that

$$c_* = \frac{\Gamma_\infty}{k}\left(\exp\frac{\sigma_\circ - \sigma}{\Gamma_\infty RT} - 1\right) = c_*(\sigma, T). \tag{43}$$

On the other hand, equation (39) makes it possible to determine the function $J(\rho, c, \sigma, T, w)$

$$J = \frac{\rho\Lambda}{\rho+\Lambda}\frac{c-c_*}{(\varsigma\Gamma(c_*) - cm)}.$$

After determining the coefficient in the differential form (41) at $d\sigma$, we can integrate the form (41) once with respect to $\sigma$, and thereby isolate in the chemical potential the dependence on the surface tension in the explicit form.

Equations (18) describe an arbitrary regime of self-consistent motion of particles and the gradient field of the admixture concentrations acting on them, which changes as a result of this motion. For the case of low velocities in the isothermal case at $p = \text{const}$, we can isolate, in system of equations (18), the solutions of the type

$$\begin{aligned} \mathbf{v} &= 0, \\ \frac{\partial \mathbf{w}}{\partial t} + \frac{\rho_l}{\rho_s}\rho B_{11}\mathbf{w} &= -\varsigma\frac{J}{\rho_s}\nabla\sigma, \\ \frac{\partial(c\rho)}{\partial t} + \operatorname{div}\left(\rho_s c_s \mathbf{w} - \frac{B_{33}}{T^2}\nabla\mu_1\right) &= 0, \\ \frac{\partial J}{\partial t} + \operatorname{div}(J\mathbf{w}) &= 0. \end{aligned} \tag{44}$$

Equations (44) are closed by the relations

$$\begin{aligned} c_s = c + \frac{\rho}{mJ}\frac{\Lambda}{\Lambda+\rho}(c-c_*), \qquad \rho_s &= mJ, \\ \mu_1 = \mu_1(c, c_*, \rho, T, \mathbf{w}), \\ \sigma = \sigma_\circ - \Gamma_\infty RT\ln\left(1 + \frac{k}{\Gamma_\infty}c_*\right), \end{aligned}$$

in which the function $c_*$ is determined from the equation

$$c_*^2 + c_*\left[\frac{\Gamma_\infty}{k} - c + \Gamma_\infty J\varsigma\left(\frac{1}{\rho}+\frac{1}{\Lambda}\right)\right] - \frac{\Gamma_\infty}{k}c = 0.$$

# REFERENCES

1. Yu.A. Minayev, On the effect of change in the particle velocity in the concentration field, *Zh. Fiz. Khim.* **C** (N9), 2379–2380 (1968).
2. V.G. Levich, *Physico-Chemical Hydrodynamics*, 700 pages, Fizmatgiz, Moscow, (1959).
3. L.D. Landay and E.M. Lifshits, *Fluid Mechanics*, Pergamon Press, New York, (1989).
4. V.N. Dorovsky, Mathematical models of two-velocity media, *Mathl. Comput. Modelling* **21** (7), 17–28 (1995).
5. S.J. Puttermann, *Superfluid Hydrodynamics*, North Holland, (1974).